

# Optical characterization of As-Ge-S thin films

A. V. STRONSKI\*, M. VLCEK<sup>a</sup>, I. D. TOLMACHOV, H. PRIBYLOVA<sup>a</sup>

*V. Lashkarev Institute of Semiconductor Physics NAS Ukraine*

<sup>a</sup>*Faculty of Chemical Technology, University of Pardubice, Pardubice, Czech Republic*

Optical characterization of  $\text{As}_{12.6}\text{Ge}_{23.8}\text{S}_{63.6}$  thin films was made from transmission spectra measurements using Swanepoel method. Spectral dependences of refractive index were well described by single oscillator model. Raman spectra of initial bulk glasses and evaporated films have shown the presence of the nanoscale intrinsic heterogeneities. Nonlinear optical properties of the films were estimated from optical parameters using different approaches and they were found to be more than two orders of magnitude higher than those of silica glasses.

(Received October 1, 2009; accepted November 12, 2009)

*Keywords:* Chalcogenide glasses, Thin films, Non-linear optical properties, Raman spectra

## 1. Introduction

Chalcogenide glassy semiconductors are intensively investigated nowadays as perspective materials for a broad range of applications in such areas as optical data storage, optoelectronics, holography etc. This is due to their unique physical and optical properties such as transmission in near IR spectral region, various photoinduced phenomena, high nonlinear optical properties. As shown in paper [1] third order non-linear susceptibility of chalcogenide glasses may be more than two orders of magnitude higher than of silica glass. Therefore study of optical properties of these materials is of great interest due to the possible applications in all-optical signal processing and integrated all-optical devices.

Direct measurement of non-linear optical properties is an elaborate procedure that requires quite complicated equipment. These difficulties can be avoided by using one of the semiempirical relations proposed in literature [2-4] for the evaluation of non-linear optical properties from linear ones.

In the present work optical properties of  $\text{As}_{12.6}\text{Ge}_{23.8}\text{S}_{63.6}$  thin films were studied using transmission measurements and Swanepoel method of refractive index determination. Non-linear optical properties of material were estimated using different approaches proposed in literature. Difference in the structure of initial bulk glass and evaporated films was studied using Raman spectroscopy.

## 2. Experimental

Glasses of composition  $\text{As}_{12.6}\text{Ge}_{23.8}\text{S}_{63.6}$  were prepared by conventional melt-quenched technique. After synthesis ampoules were water-quenched. Thin films were prepared by thermal vacuum evaporation onto the glass substrate under room temperature.

Raman spectra of bulk glasses and thin films were

measured using Fourier spectrophotometer Bruker IFS55 Equinox with FRA-106 attachment. Nd-YAG laser light at wavelength of  $1.06\ \mu\text{m}$  was used for excitation.

The normal-incidence transmission spectra of the films were measured at room temperature in the range of  $0.4\text{-}2.5\ \mu\text{m}$ . Optical characterization of the films was done using the method proposed by Swanepoel [5]. The above mentioned method allows determination of the film thickness and optical properties from transmission spectrum only with high accuracy by drawing the envelopes of the spectrum.

## 3. Results and discussion

Transmission spectrum of studied film is presented in fig. 1 along with computer drawn envelopes. There is broad transparency region at long wavelengths and significant drop of transparency in the region of  $400\text{-}600\ \text{nm}$  due to the increase of absorption.

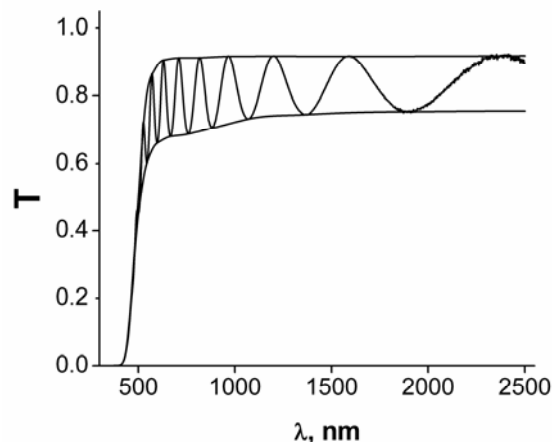


Fig. 1. Transmission spectrum of  $\text{As}_{12.6}\text{Ge}_{23.8}\text{S}_{63.6}$  thin film provided with computer drawn envelopes

Spectral dependence of refractive index calculated together with films thickness by Swanepoel method [5] is given in the fig. 2. Solid line corresponds to the least-squares fitting of this dependence to the function

$$n(\lambda) = \frac{a}{\lambda^2} + c \quad (1)$$

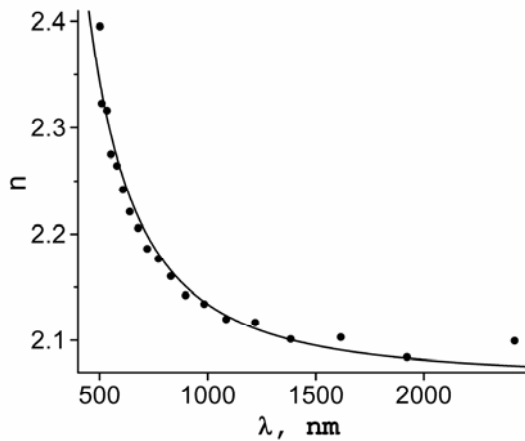


Fig. 2. Spectral dependence of the refractive index of  $As_{12.6}Ge_{23.8}S_{63.6}$  thin film determined by Swanepoel method

Spectral dependence of refractive index can be well described by single oscillator model [6]. According to this model refractive index is related to energy of incident photon by equation

$$n^2 - 1 = \frac{E_d E_0}{E_0^2 - E^2} \quad (2)$$

where  $E_0$  is single oscillator energy,  $E_d$  is dispersion energy. In this expression  $E_0$  determines the position of effective oscillator connected with average energy gap;  $E_d$  is the dispersion energy characterizing the strength of interband transitions. Expression (2) was successfully applied for the analysis of dispersion data for more than hundred of different materials: covalent and ionic, crystalline and amorphous [6]. To obtain  $E_0$  and  $E_d$  we plotted dependence

$$(n^2 - 1)^{-1} = f(E^2) \quad (3)$$

at the points corresponding to the extremes on the transmission spectrum and then performed least squares fitting to the straight line (see fig. 3). It can be seen that points corresponding to maximum photon energy were dropped out from the straight linear dependence, therefore they were excluded from consideration during evaluation  $E_d$  and  $E_0$  parameters.

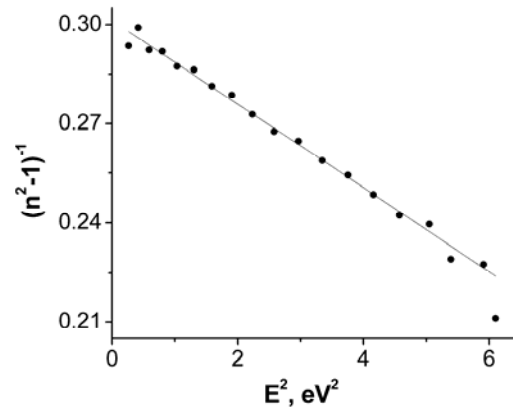


Fig. 3. Plot of the refractive index factor,  $(n^2 - 1)^{-1}$ , versus the photon energy squared,  $E^2$ , to determine values of  $E_d$  and  $E_0$

Optical band gap  $E_g$  was also determined. It can be obtained either from Tauc law,  $(\alpha\hbar\omega)^{1/2} = f(E)$ , or using dependence  $\alpha = f(E)$ . In paper [7] it was stated that difference in value  $E_g$  would be up to 10 - 20% from one method to another. For the present type of materials one should prefer Tauc law [7]. In fig. 4 energy dependence of  $(\alpha E)^{1/2}$  parameter is plotted. Linear range in the region of high photon energies corresponds to the Tauc law. Energy band gap is the point where this line intersects with abscissa (see fig. 4).

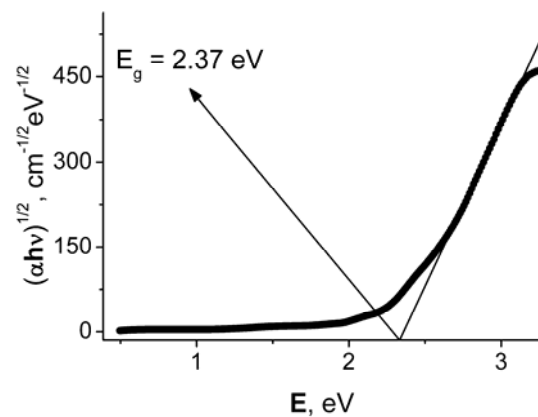


Fig. 4. Determination of optical band gap,  $E_g$ , of  $As_{12.6}Ge_{23.8}S_{63.6}$  thin film from Tauc plot

In Fig. 5 the absorption coefficient (in logarithmic scale) versus incident photon energy is plotted. Almost linear region where absorption coefficient ranges from  $2 \cdot 10^2$  to  $5 \cdot 10^3 \text{ cm}^{-1}$  obeys Urbach's law:

$$\alpha(E) = \alpha_0 \exp\left(\frac{E}{E_c}\right) \quad (4)$$

Optical parameters evaluated from transmission spectra together with thickness  $d$  are given in the Table 1.  $E_d$  and  $E_0$  stands for dispersion energy and single oscillator energy,  $E_g$  is optical band gap,  $E_c$  is Urbach energy,  $n_0$  is refractive index in the limit  $E \rightarrow 0$ . It can be seen from the data given in this table that  $E_0$  scales well with the optical band gap ( $E_0 \approx 2 \times E_g$ ).

Raman spectroscopy is one of the commonly used ways to investigate structure of amorphous materials and may provide useful information on the origin of optical nonlinearities as well as on structural changes within the material during its vacuum evaporation.

Table 1. Optical parameters obtained from transmission spectra.

Film No.	$d$ , nm	$E_d$ , eV	$E_0$ , eV	$E_g$ , eV	$E_c$ , eV	$n_0$
1	1132	16.5	4.9	2.36	0.14	2.08
2	1152	16.2	4.9	2.36	0.15	2.08
3	1164	15.8	4.8	2.40	0.15	2.07
4	1158	15.8	4.9	2.37	0.15	2.06
5	1151	16.1	5.0	2.36	0.15	2.06
6	1142	16.0	5.0	2.35	0.15	2.06
mean	1150	16.1	4.9	2.37	0.15	2.07

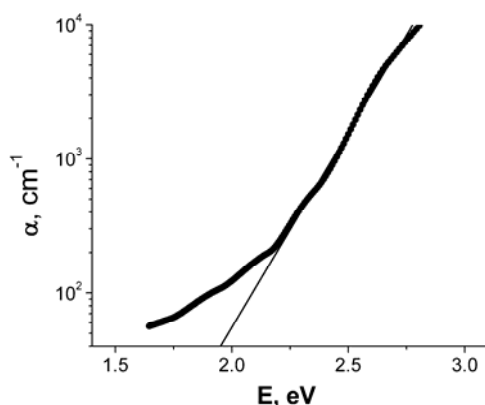


Fig. 5. Urbach absorption tail of  $As_{12.6}Ge_{23.8}S_{63.6}$  thin film

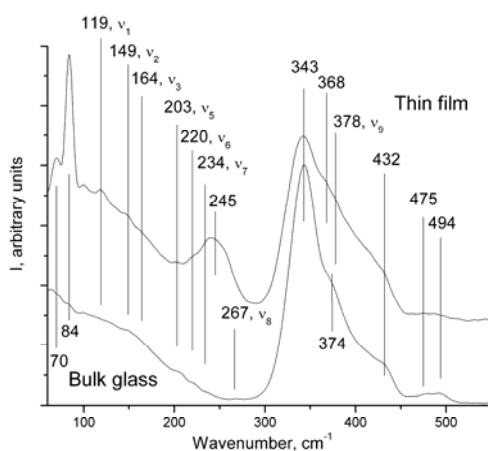


Fig. 6. Raman spectra of  $As_{12.6}Ge_{23.8}S_{63.6}$  initial bulk glass and thin film.

Raman spectrum of the fresh evaporated films along with the initial bulk glass spectrum is presented in fig. 6. The main differences of bulk glass Raman spectrum compared to thin films' spectrum constitutes in disappearing of a broad double band near  $240 \text{ cm}^{-1}$  and also in increasing of  $432 \text{ cm}^{-1}$  shoulder's intensity. Peaks at  $368$  and  $378 \text{ cm}^{-1}$  merge into one peak at  $374 \text{ cm}^{-1}$ .

The most intensive peak at  $343 \text{ cm}^{-1}$  observed either in thin film spectra or in bulk glass spectra consisted of two overlapped parts originated from pyramidal  $AsS_3$  and tetrahedral  $GeS_4$  units which constitute structural backbone of the glass [8]. The shape of this peak in the film spectrum is more diffuse which points on higher degree of chemical disorder in evaporated films compared to initial glasses. A certain amount of  $As_4S_4$  monomers is present in the film as indicated by the presence of low-frequency modes  $\nu_1 - \nu_3$  and  $\nu_5 - \nu_7$  and also,  $\nu_9$  mode in the film spectrum. The bulk glass spectrum also contains mode  $\nu_8$  which is characteristic mode of  $As_4S_3$  monomers [9].

Peak at  $368 \text{ cm}^{-1}$  in thin film spectrum and peak at  $374 \text{ cm}^{-1}$  in the bulk glass spectrum correspond to the so-called  $A_1^C$  companion mode. These peaks can be ascribed to the oscillations of edge-shared (ES) tetrahedra or medium range order structures consisted of  $AsS$  pyramids along with corner shared (CS) or ES tetrahedra  $GeS$  [8]. Mode at  $432 \text{ cm}^{-1}$  can be related to the vibrations of ES tetrahedra or S-S dimmers at the edge of clusters.

A broad band near  $245 \text{ cm}^{-1}$  was observed earlier in Raman spectra of  $Ge_xAs_{40-x}S_{60}$  glasses for  $x$  values higher than 24 [9]. As pointed by authors of [9] the emerging and ascending of  $245 \text{ cm}^{-1}$  band with raising  $x$  number was a result of increasing the ratio of Ge-Ge vs. As-As bond concentration. The Ge-Ge bonds was stated to be found either in  $Ge_2S_{6/2}$  ethanlike units or in  $Ge-S_{4-n}Ge_n$  tetrahedra.

The two overlapped peaks at 237 and 256  $\text{cm}^{-1}$  was also observed in Raman spectra of glassy  $\text{GeS}_2$  obtained under certain technological conditions [10]. Numerical calculations provided by authors [10] showed that although line at 256  $\text{cm}^{-1}$  can be ascribed to oscillations in the ethane-like nanophase whereas the 237  $\text{cm}^{-1}$  peak only present in vibration modes of three-fold coordinated GeS structures. Therefore modes at 237 and 256  $\text{cm}^{-1}$  were ascribed to oscillations in three-fold coordinated GeS structures. As pointed by authors [10], these structures may exist in the glass matrix in the form of crystalline  $\text{GeS}_2$  nanophase of about 7 – 12 Å in size.

Modes at 70, 84, 494  $\text{cm}^{-1}$  are related to vibrations of covalent S-S bonds. A weak traces of  $\text{S}_8$  rings can be found in bulk glass as well as in evaporated film. They have vibrational modes at 150, 220 and 474  $\text{cm}^{-1}$ . Whereas line observed at 220  $\text{cm}^{-1}$  can be ascribed to different structural units, the 475  $\text{cm}^{-1}$  mode is characteristic of  $\text{S}_8$  rings.

Non-linear optical properties were estimated by two different ways from linear optical properties which were calculated from transmission spectra.

In paper [3] for the purpose of estimation of non-linear properties of chalcogenide glasses a generalized Miller's rule was used which establishes relation between linear optical susceptibility,  $\chi^{(1)}$ , and third order non-linear optical susceptibility,  $\chi^{(3)}$ . According to this rule:

$$\chi^{(3)} \cong A(\chi^{(1)})^4. \quad (5)$$

Here A is a constant. It's value for chalcogenides appears to be  $A = 1.7 \cdot 10^{-10}$  and at that we obtain value of  $\chi^{(3)}$  in esu. Authors made a comparison between estimated and experimentally measured values and achieved satisfactory agreement better than an order of magnitude.

An authors of [4] proposed to use a classical anharmonic oscillator model to establish correlation between  $\chi^{(3)}$  and  $E_g$ :

$$\chi^{(3)} \cong B \frac{1}{E_g^6} \left[ 1 - \left( \frac{h\nu}{E_g} \right)^2 \right]^{-4}, \quad (6)$$

where  $h\nu$  is photon energy,  $B = 2.846 \cdot 10^{-16} \text{ esu} \cdot (\text{eV})^6$  is constant. Values of  $n_2$  and  $E_g$  were measured independently and plotted in the form of function

$$n_2 = f \left( \frac{1}{E_g^6} \left[ 1 - \left( \frac{h\nu}{E_g} \right)^2 \right]^{-4} \right), \quad (7)$$

for silica glasses, some oxides and chalcogenides representing results either obtained by authors of the work or cited after the other publications. All data were fitted well by the straight line.

Values of  $n_2$  and  $\chi^{(3)}$  obtained using formulas (5) and (6) (in the long wavelength limit) are shown in table 2. Results coincide within an order of magnitude but values obtained from generalized Miller's rule are about 50% higher then those obtained from anharmonic oscillator model. Non-linear optical parameters of studied films are more than two orders of magnitude higher then those of silica glass ( $2.2 \cdot 10^{-16} \text{ cm}^2/\text{W}$  [12]).

Table 2. Estimated non-linear properties.

Film No.	$\chi^{(3)}$ , $10^{-12}$ esu		$n_2$ , $10^{-11}$ esu	
	Miller's rule	anharmonic oscillator	Miller's rule	anharmonic oscillator
1	0.85	0.46	1.54	0.82
2	0.83	0.44	1.50	0.83
3	0.79	0.4	1.44	0.74
4	0.75	0.43	1.37	0.79
5	0.74	0.45	1.35	0.82
6	0.74	0.46	1.35	0.84
<b>mean</b>	<b>0.78</b>	<b>0.44</b>	<b>1.43</b>	<b>0.81</b>

As discussed in [11] besides contribution to the polarizability from the electron lone pairs other factors such as glass structure or density, the presence of unpaired electrons and the present of defect states must be taken

into account. For example in Ge-As-S(Se) glasses the situation with the presence of the different structural units is further complicated by the opportunity for the both homopolar (for example, As-As, Ge-Ge) and heteropolar

(Ge-S(Se), As-S(Se)) bonds that lead to a variety of “defect” gap states which can contribute to the nonlinearity. Above presented data of Raman spectra of studied glasses and films also show the presence of such phase separation.

High values of non-linear optical parameters shows that such media are perspective for the use in optical switchers, frequency converters, electrooptical modulators and all-optical signal processing devices.

#### 4. Conclusions

Optical properties of the Ge-As-S films were investigated. It was shown that spectral dependence of the refractive index for studied Ge-As-S films is well described by single oscillator model. Parameters of the single oscillator model, optical band gap  $E_g$ , Urbach energy were determined. Raman spectra of bulk glasses and thin films suggests the presence of phase separation that lead to a variety of “defect” gap states which can contribute to the nonlinearity. Estimation of the non-linear properties of studied films have shown them to be more than two orders of magnitude higher than those of silica glass, which makes them perspective in such applications as ultra-fast optical switching, frequency converters, electro-optical modulators and all-optical signal processing.

#### Acknowledgement

H. P. and M.V. thanks the Czech Ministry of Education, Youth and Sports for support under Grant 0021627501.

#### References

- [1] J. M. Harbold, F. O. Ilday et al, IEEE Photonics Techn. Let. **14**(6), 822 (2002).
- [2] K. Petkov, P. J. S. Ewen, J. Non-Cryst. Solids **249**, 150 (1999).
- [3] H. Ticha, L. Tichy, J. Optoelectron. Adv. Mater. **4**(2), 381 (2002).
- [4] J. S. Sanghera, C. M. Florea, L. B. Shaw, et al, J. Non-Cryst. Solids **354**, 462 (2008).
- [5] R. Swanepoel, J. Phys. E: Sci. Instrum. **16**, 1214 (1983).
- [6] S. H. Wemple. Phys. Rev. B **7**(8), 3767 (1973).
- [7] E. R. Skordeva, J. Optoelectron. Adv. Mater. **1**(1), 43 (1999).
- [8] E. Vateva, E. Skordeva, J. Optoelectron. Adv. Mater. **4**(1), 3 (2002).
- [9] S. Mamedov, D. G. Georgiev, et. al. J. Phys.: Condens. Matter **15**, S2397 (2003).
- [10] R. Holomb, P. Johansson, et. al. Phil. Mag., **85**(25), 2947 (2005).
- [11] J. T. Gopinath, M. Soljasic et al. J. Appl. Phys **96**(11), 6931 (2007).
- [12] V. G. Ta'eed, N. J. Baker, L. Fu, et. al. Opt. Express, **1**(15), 9205 (2007).

---

\*Corresponding author: stronski@isp.kiev.ua